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Doidge et al.

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[54] **ORGANOCLAYS**

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[*] Notice: The portion of the term of this patent subsequent to Nov. 18, 2003 has been disclaimed.

[21] Appl. No.: **930,279**

[22] Filed: **Nov. 12, 1986**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 727,022, Apr. 25, 1985, Pat. No. 4,623,398.

[51] **Int. Cl.**⁴ **C04B 14/00;** C04B 33/00

[52] **U.S. Cl.** .... **106/308 N;** 106/309; 501/145; 501/148; 501/149

[58] **Field of Search** .... 106/308 N, 287.25; 252/315.5, 315.6; 501/147

[56] **References Cited**

U.S. PATENT DOCUMENTS

4,412,018 10/1983 Finlayson et al. 106/287.25

4,623,398 11/1986 Goodman et al. 501/148

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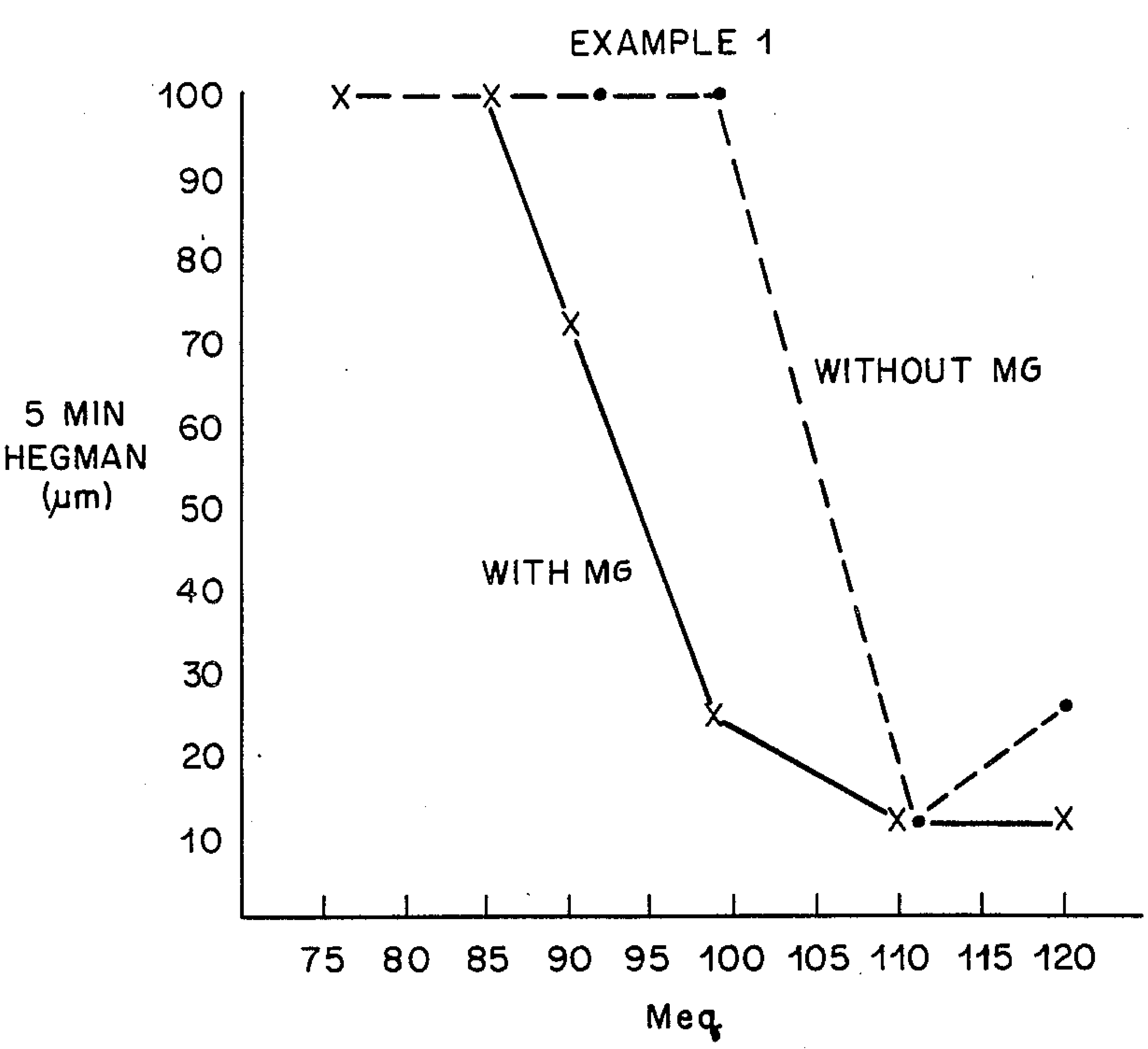
[57] **ABSTRACT**

An organoclay is prepared by mixing a quaternary ammonium compound with an aqueous suspension of a smectite clay in proportions such that there are present from 75 to 110 milliequivalents of quaternary ammonium cation per 100 g of dry smectite clay, thereafter subjecting the smectite clay/quaternary ammonium compound/water mixture to high shear mixing for a time sufficient to dissipate in the mixture at least 100 KJ of energy per kg. of dry solids in the mixture; and then dewatering the product thus obtained.

9 Claims, 2 Drawing Sheets



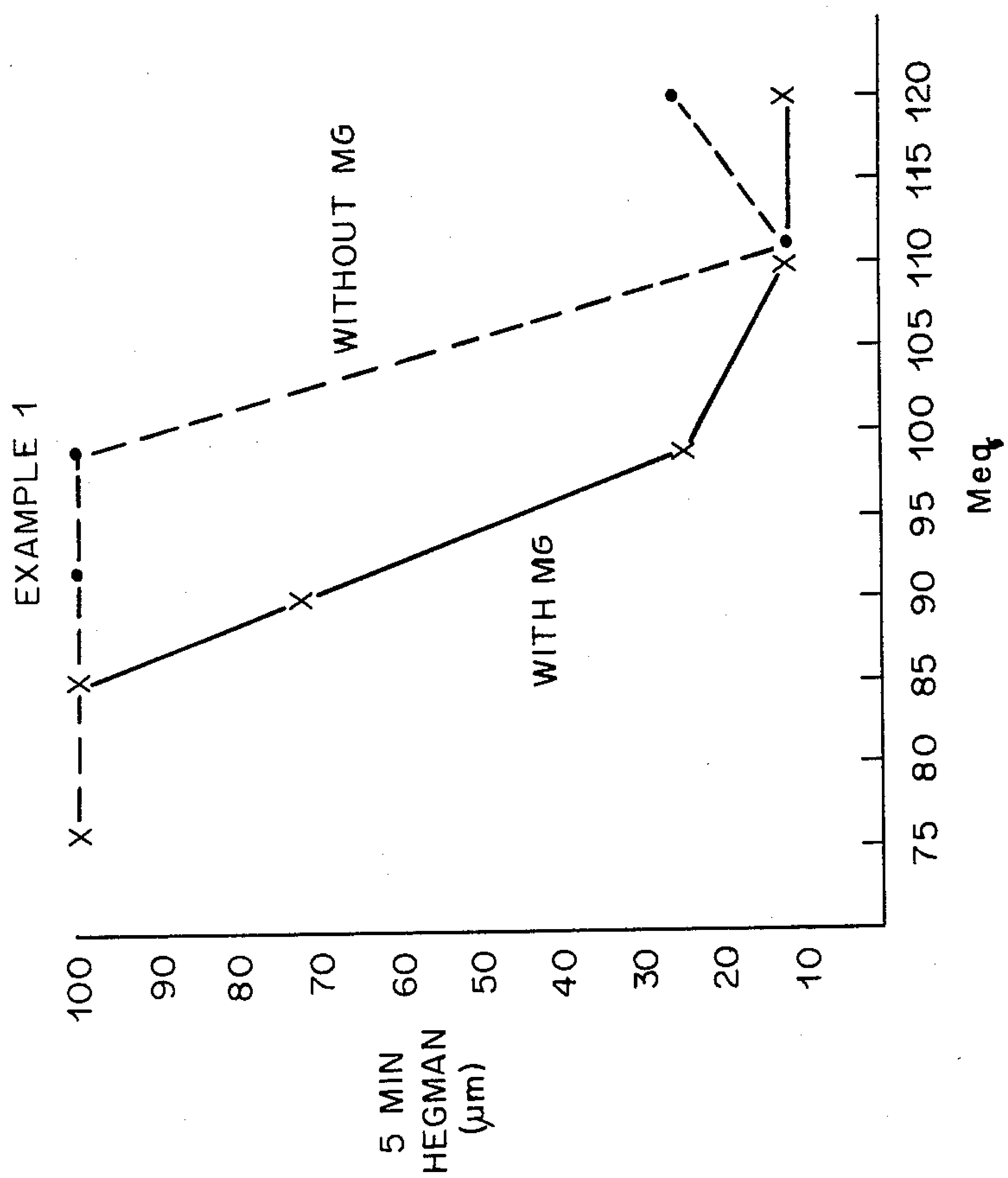

EXAMPLE 1
WITHOUT MG
WITH MG
75 80 85 90 95 100 105 110 115 120
Meq
100 90 80 70 60 50 40 30 20 10
5 MIN
HEGMAN
(μm)

FIG. 1

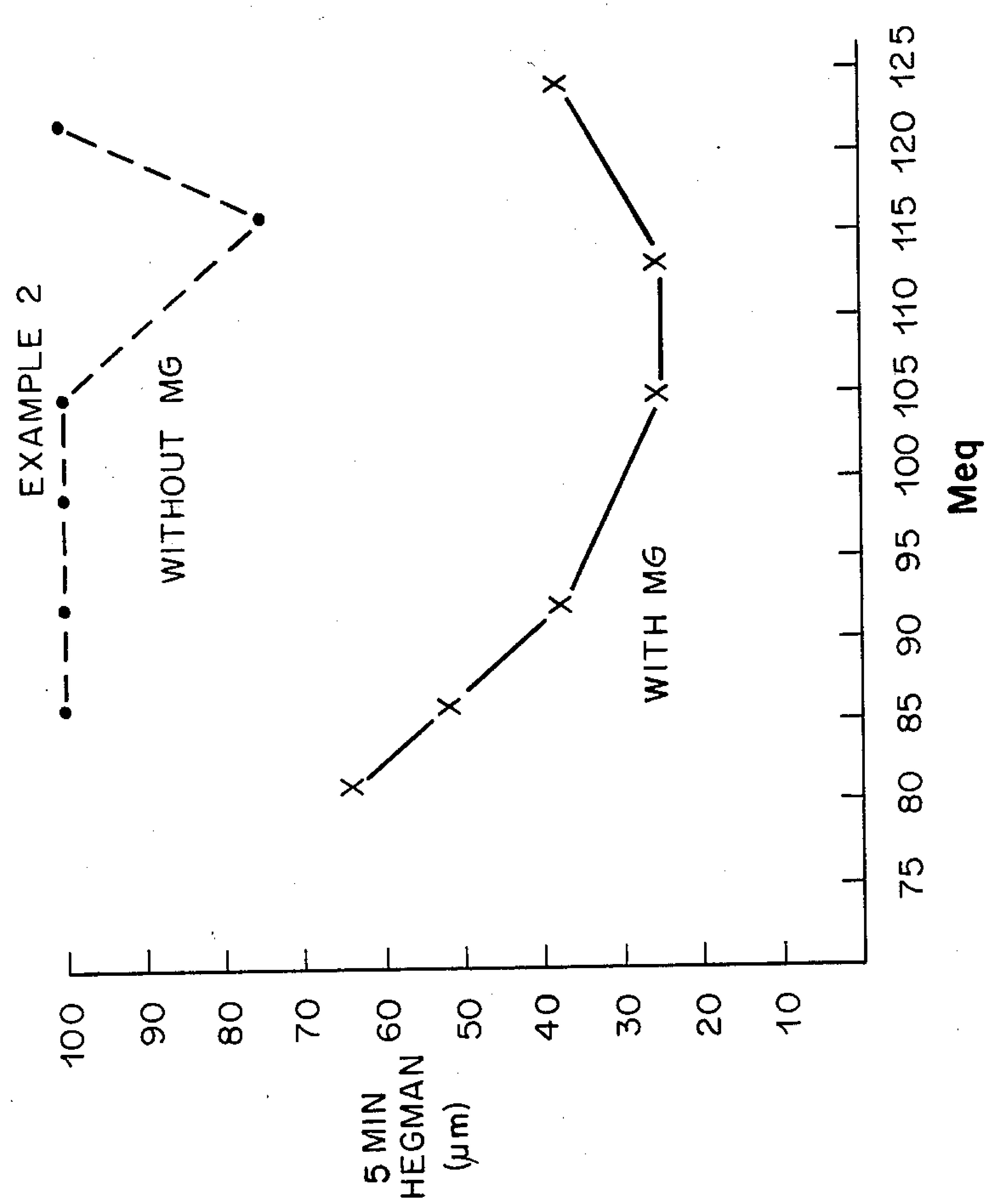

EXAMPLE 2
WITHOUT MG
WITH MG
5 MIN
HEGMAN
(μm)
100
90
80
70
60
50
40
30
20
10
75
80
85
90
95
100
105
110
115
120
125
Meq

FIG. 2

ORGANOCLAYS

This application is a continuation-in-part of U.S. Ser. No. 727,022, filed Apr. 25, 1985 now U.S. Pat. No. 4,623,398.

BACKGROUND OF THE INVENTION

This invention relates to a process for preparing organoclays and to the products of such a process.

An organoclay is an organophilic cation-modified clay derived from a clay mineral, generally of the smectite group, for example, bentonite, montmorillonite, hectorite, saponite or the like, by replacing the inorganic exchangeable cations, generally alkali or alkaline earth metal cations, which occur in the natural clay mineral, by organic cations each comprising at least one hydrocarbon radical which has sufficient carbon atoms to render the surface of the cation-exchanged clay hydrophobic.

Organoclays have been found to be very useful as thixotropic agents in organic media such as, for example, lubricating greases, oil-based drilling fluids, paints, varnishes, enamels and printing inks. However, an organoclay is, in general, difficult to disperse in an organic medium to form the uniform gel structure which is required to thicken, or to increase the viscosity of the organic medium. Even where sufficient dispersibility occurs to yield a satisfactory gel structure, small quantities of undispersed particles can be deleterious, such as in paints. Various means have been used to improve the dispersibility of an organoclay in an organic medium including the use of a polar organic material, such as a low molecular weight alcohol or ketone, as a dispersing aid, and the use of an excess of a specially selected organic cation in the preparation of the organoclay.

It is an object of the present invention to prepare an organoclay which has improved dispersibility as measured by the Hegman Gauge.

It is a further object of this invention to prepare an organoclay which will disperse readily in an organic medium to form a homogeneous gel structure.

SUMMARY OF THE INVENTION

According to the present invention there is provided a process for preparing an organoclay which is readily dispersible in an organic medium, which process comprises:

(a) mixing an aqueous suspension of a clay of the smectite group with a quaternary ammonium compound capable of rendering the smectite group clay organophilic in proportions such that there are present from 75 to 110 milliequivalents of quaternary ammonium cation per 100 g of dry smectite clay;

(b) subjecting the mixture formed in step (a) to mixing at high shear for a time sufficient to dissipate in the mixture at least 100 KJ of energy per kg. of dry solids in the mixture; and

(c) dewatering the product of step (b). Preferably, the dewatered product of step (c) is dried and milled.

In step (a) the quaternary ammonium compound is preferably one which can be represented by the general formulae:

$$\left[\begin{array}{c} R_1 \\ | \\ R_4-N^+-R_2 \\ | \\ R_3 \end{array}\right] X^-$$

wherein R_1 is a saturated or unsaturated alkyl group having from 10 to 24 carbon atoms, R_2 and R_3, which may be the same or different, are each a saturated or unsaturated alkyl group having from 1 to 24 carbon atoms or an aralkyl group having at least 7 carbon atoms, R_4 is an alkyl group having from 1 to 6 carbon atoms or an aralkyl group having at least 7 carbon atoms, and X is OH, Cl, Br, I, NO_2, CH_3SO_4 or $CH_3.COO$.

Examples of such compounds are the benzyl methyl dialkyl ammonium chlorides, the dimethyl dialkyl ammonium chlorides, the benzyl dimethyl alkyl ammonium chlorides, the benzyl trialkyl ammonium chlorides and the methyl trialkyl ammonium chlorides, where the one or more alkyl group is a mixture of hydrocarbon radicals derived from tallow and having from 14 to 20 carbon atoms but in which C_{18} radicals preferably predominate. (A typical analysis of such a mixture of hydrocarbon radicals contained in tallow is: C_{14} 2.0%; C_{15} 0.5%; C_{16} 19.0%; C_{17} 1.5%; C_{18} 66.0% and C_{20} 1.0%). The hydrocarbon radicals may be partially unsaturated, as in natural tallow, or may be substantially completely saturated as a result of treating the tallow with hydrogen in the presence of a suitable catalyst. For the present invention it has been found particularly advantageous to use a mixture of dimethyl dihydrogenated tallow ammonium chloride and dimethyl benzyl hydrogenated tallow ammonium chloride.

The mixing at high shear is preferably effected by passing the suspension through a homogenizer of the type in which the suspension is forced in the form of a thin film edgewise through a thin, hard-surfaced gap under a pressure of at least 250 pounds per square inch (1.7 MPa) and at high velocity. A suitable homogeniser is described in British Patent Specification No. 987,176 and in U.S. Pat. Nos. 3,039,703 and 3,162,379). Such a homogenizer is manufactured by the Manton-Gaulin Company. Advantageously the homogenizer is operated at a pressure of at least 1500 pounds per square inch (10.5 MPa). The amount of energy E, in KJ per kg. of dry solids, dissipated in the mixture is given by the expression

$$E = \frac{nP \cdot 10^3}{w}$$

where P is the pressure in MPa exerted in the Manton-Gaulin (MG) homogenizer, n is the number of passes through the Manton-Gaulin homogenizer, and w is the weight in grams of dry solids in one liter of the aqueous mixture.

The suspension of the clay is mixed with the quaternary ammonium compound in proportions such that there are present from 75 to 110 milliequivalents of quaternary ammonium cation per 100 g of dry clay.

Thus, it has now been found that on an economic basis an advantage exists whereby increased dispersibility can be achieved at lower expense by homogenization of the character described above of lower milliequivalent organoclays (75 to 110 Meq) rather than increasing the Meq levels with excess quaternary ammonium compound which is costly. Further and for a given Meq level upon the organoclay, use of the invention will provide a product with faster dispersion.

As will be shown in the Examples and the figures, post homogenization, as with a Manton-Gaulin mill, of these organoclay slurries, clearly improves dispersibility of the organoclays.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1 and 2 are graphs which illustrate, respectively for Examples 1 and 2, the relationship between Meq and the five minute Hegman grind gauge readings of the organoclays with and without treatment in a Manton-Gaulin homogenizer.

DETAILED DESCRIPTION

The invention is illustrated by the following Examples.

EXAMPLE I

Organoclay samples were prepared by the following method.

Crude Wyoming sodium bentonite was mixed using a Cowles dissolver for one hour with sufficient water to form a bentonite/water suspension of 8.0 wt. % solids. After allowing it to stand for a period of sixteen hours, the suspension was passed through a No. 200 USA Standard Testing Sieve (aperture 0.075 mm). The undersize fraction (approximately 6 wt. % solids) was then subjected to particle size separation using a Delaval nozzle discharge, disc centrifuge at a flow rate of approximately 2.0 liters per minute. The fine fraction (approximately 4 wt. % solids) was then passed through a Manton-Gaulin homogenizer at a pressure of 4000 psi (27.6 MPa).

In each case, 2,500 g of the clay slurry was heated with the aid of a water bath to 65° C. To the heated slurry was then added the calculated weight of the quaternary ammonium compound and isopropyl alcohol (in which form the quaternary ammonium compounds are available commercially). In this Example, dimethyl dihydrogenated tallow ammonium chloride with a molecular weight of 576.6 and an activity of 74.8% was used. Six organoclays were produced ranging from 76–120 milliequivalents quaternary ammonium cation per 100 g of dry bentonite.

The resultant mixtures were then stirred using a Lightnin Model 20 variable speed mixer for 30 minutes, filtered on a Buchner funnel, washed with hot water and dried in a Blue M forced air oven at 55° C. for sixteen hours. The dry products were then milled using a Fritsch pulversette to a particle size of 98 wt. % passing through a No. 200 USA Standard Testing Sieve (aperture 0.075 mm). This series of six organoclays was designated numbers 1–6.

A second series of six organoclays was prepared using the above procedure with the exception that prior to filtration the reacted organoclay slurries were passed once through the Manton-Gaulin homogenizer at a pressure of 4000 psi (27.6 MPa). All other preparation procedures were as described above. These six organoclays were designated numbers 1A–6A.

The twelve organoclays thus prepared and now designated 1–6 and 1A–6A were then tested for ease of dispersion in a white gloss enamel paint formulation I, shown below. Each organoclay was added to the latter stage of the grind phase after pigment dispersion. Each organoclay was stirred into the paint using a Cowles type blade of 41.28 mm diameter at 5000 rpm for 20 minutes. During the mixing operation small samples were taken on a spatula and spread on a Hegman grind gauge. Hegman grind gauge readings were recorded every 5 minutes.

A large sample of each completely mixed paint was allowed to stand for 24 hours and measurements of the viscosity of the paints at 22° C. were then made using (a) a Brookfield Viscometer spindle 4 at 0.5, 5 and 50 rpm respectively and (b) a Stormer Viscometer—(using 250 g).

In addition, the following other test procedures were conducted: Leneta sag and leveling and Gloss at 20°, 60° and 85° using a Pacific Scientific Gardener Glossometer.

The results obtained are set forth in Tables 1 and 1A.

EXAMPLE 2

Organoclay samples were prepared by the following method.

Crude Wyoming sodium bentonite was mixed using a Cowles dissolver for one hour with sufficient water to form a bentonite/water suspension of 6.0 wt. % solids. After allowing it to stand for a period of sixteen hours the suspension was passed through a No. 200 USA Standard Testing Sieve (aperture 0.075 mm). The undersize fraction (approximately 4.5 wt. % solids) was then subjected to particle size separation using a Delaval nozzle discharge, disc centrifuge at a flow rate of 2.0 liters per minute. To this fine fraction which is approximately 3.0 wt. % solids, was added 2.0% by weight based upon the dry weight of bentonite of sodium carbonates, a sodium exchange salt. The fine fraction was then passed through the Manton-Gaulin homogenizer three times at 4000 psi (27.6 MPa).

In each case, 2500 g of the clay slurry was heated with the aid of a water bath to 65° C. To the heated slurry was then added a mixture of a quaternary ammonium compound and isopropyl alcohol comprising 87 mole % dimethyl dihydrogenated tallow ammonium chloride and 13 mole % dimethyl benzyl hydrogenated tallow ammonium chloride, the average molecular weight of the blend being 556 with an activity of 75.7%. Six organoclays were produced with a range of milliequivalents of quaternary ammonium cation per 100 g of dry bentonite. The resultant mixtures were then stirred using a Lightnin Model 20 variable speed mixer for 30 minutes, filtered on a Buchner funnel, washed with hot water and dried in a Blue M forced air oven at 55° C. for sixteen hours. The dry product was then milled using a Fritsch pulversette to a particle size of 98.0 wt. % passing through a No. 200 USA Standard Testing Sieve (aperture 0.075 mm). This series of organoclays was designated numbers 7–12.

A second series of six organoclays was prepared using the above procedure with the exception that prior to filtration the reacted organoclays were passed once through the Manton-Gaulin homogenizer at a pressure of 4000 psi (27.6 MPa). All other preparation procedures were as described above. These organoclays were designated numbers 7A–12A.

The twelve organoclays thus prepared and now designated 7–12 and 7A–12A were then tested for ease of dispersion in a white gloss top coat enamel paint formulation II, shown below. Each organoclay was added to the latter stage of the grind phase. During the mixing operation small quantities were taken on a spatula and spread on a Hegman grind gauge. Hegman grind gauge readings were recorded every 5 minutes. This data clearly shows that use of the invention improves the rate of dispersion as measured by the Hegman test, without degrading the other important paint properties tabulated.

A large sample of each completely mixed paint was allowed to stand for 24 hours and measurements of the viscosity of the paints at 22° C. were then made using (a) a Brookfield Viscometer spindle 4 at 0.5, 5 and 50 rpm respectively, and (b) a Stormer Viscometer (using 450 g). In addition the following other test procedures were conducted: Leneta sag and leveling and Gloss at 20°, 60° and 85° using a Pacific Scientific Gardener Glossometer.

The results obtained are set forth in Tables 2 and 2A.

TABLE 1

WITHOUT MG TREATMENT

ORGANOCLAY SAMPLE	MEQ OF CATION PER 100 g OF CLAY	HEGMAN GAUGE READINGS LARGEST PARTICLES (MICROMETERS) INCLUDING NUMBER OF SPECKS (IN PARENTHESES) 5 MIN.	10 MIN.	15 MIN.	20 MIN.	24 HRS.
1	77	>100	>100	75(>10)	75(>10)	50(>10)
2	85	>100	>100	50(>10)	50(>10)	38(>10)
3	92	>100	50(>10)	25(>10)	25(>10)	20(>10)
4	99	>100	12(>10)	12(5)	12(5)	20
5	111	12(>10)	12(3)	12(5)	12(5)	12(5)
6	120	25(>10)	12(>10)	12(5)	12(5)	12(5)

ORGANOCLAY SAMPLE	24 HOUR .5	BROOKFIELD 5	VISCOSITY (rpm) 50 rpm	STORMER KU	SAG/LEVELING LENETA (MLS)	GLOSS 20°	60°	85°
1	16000	4000	1544	87	10/3	50.0	85.1	91.0
2	18000	4240	1600	90	10/3	46.5	87.1	91.5
3	21600	5200	1960	92	12/2	48.7	88.0	92.0
4	22000	4800	1590	91	12/2	40.3	84.7	90.8
5	20000	4400	1460	90	12/1	46.6	86.9	92.6
6	18000	3800	1260	90	12/3	42.4	85.6	91.3

TABLE 1A

WITH MG TREATMENT

ORGANOCLAY SAMPLE	MEQ OF CATION PER 100 g OF CLAY	HEGMAN GAUGE READINGS LARGEST PARTICLES (MICROMETERS) INCLUDING NUMBER OF SPECKS (IN PARENTHESES) 5 MIN.	10 MIN.	15 MIN.	20 MIN.	24 HRS.
1A	76	100	88	50(>10)	25(>10)	25(>10)
2A	85	100	100	38(>10)	12(5)	12(10)
3A	90	72(>10)	25(>10)	12(>10)	12(5)	12(10)
4A	99	25(>10)	12(>10)	12(5)	12(5)	12(5)
5A	110	12(>10)	12	12(5)	12(5)	12(5)
6A	120	12(>10)	12(5)	12(5)	12(5)	12(5)

ORGANOCLAY SAMPLE	24 HOUR .5	BROOKFIELD 5	VISCOSITY (rpm) 50 rpm	STORMER KU	SAG/LEVELING LENETA (MLS)	GLOSS 20°	60°	85°
1A	11600	2960	1060	87	9/4	44.6	86.4	91.5
2A	17200	3920	1336	89	12/3	46.1	87.9	90.0
3A	14000	3600	1200	87	10/3	45.0	87.2	91.3
4A	22400	5440	2004	92	12/1	45.9	87.0	93.3
5A	32000	8200	2972	103	12/1	48.9	89.0	94.0
6A	20400	5040	1700	91	12/2	48.2	88.0	92.6

TABLE 2

WITHOUT MG TREATMENT

ORGANOCLAY SAMPLE	MEQ OF CATION PER 100 g OF CLAY	HEGMAN GAUGE READINGS LARGEST PARTICLES (MICROMETERS) INCLUDING NUMBER OF SPECKS (IN PARENTHESES) 5 MIN.	10 MIN.	15 MIN.	20 MIN.	24 HRS.
7	86	>100	>100	>100	>100	64(>10)
8	92	>100	>100	75(>10)	75(>10)	64
9	99	>100	64(>10)	64(>10)	64(>10)	44
10	105	>100	85	48(>10)	48(>10)	48(5)
11	116	75(>10)	38(5)	25(>10)	25	25(5)
12	122	100	38(>10)	25(5)	12(>10)	12(5)

ORGANOCLAY SAMPLE	24 HOUR .5	BROOKFIELD 5	VISCOSITY (rpm) 50 rpm	STORMER KU	SAG/LEVELING LENETA (MLS)	GLOSS 20°	60°	85°
7	12000	4640	2644	106	8/4	67.1	90.5	95.3
8	15600	5480	2836	107	10/3	67.0	91.3	95.2
9	12000	4560	2512	105	9/4	66.7	92.2	96.2
10	20000	5920	2688	111	12/3	64.3	90.6	96.5
11	18400	4880	2048	105	12/3	64.8	91.4	96.8

TABLE 2-continued

WITHOUT MG TREATMENT								
12	20000	5680	2380	108	12/3	67.9	91.7	96.5

TABLE 2A

WITH MG TREATMENT

ORGANOCLAY SAMPLE	MEQ OF CATION PER 100 g OF CLAY	HEGMAN GAUGE READINGS LARGEST PARTICLES (MICROMETERS) INCLUDING NUMBER OF SPECKS (IN PARENTHESES) 5 MIN.	10 MIN.	15 MIN.	20 MIN.	24 HRS.
7A	81	64(>10)	64(>10)	38(>10)	38(>10)	25
8A	86	52(>10)	52(>10)	52(>10)	38(>10)	25
9A	92	38(>10)	38(>10)	25(>10)	25(>10)	12(>10)
10A	105	25(>10)	12(5)	12(5)	12(5)	12(5)
11A	113	25(5)	25(5)	12(5)	12(5)	12(5)
12A	124	38(>10)	25(5)	25(5)	12(3)	

ORGANOCLAY SAMPLE	24 HOUR .5	BROOKFIELD 5	VISCOSITY (rpm) 50 rpm	STORMER KU	SAG/LEVELING LANETA (MLS)	GLOSS 20°	60°	85°
7A	9600	4160	2456	108	8/4	74.5	98.0	98.0
8A	10400	4280	2460	107	8/5	74.8	99.2	99.2
9A	13600	5040	2716	109	9/4	73.0	97.5	97.5
10A	18400	5200	2144	108	12/3	65.0	97.0	97.1
11A	20400	5640	2344	109	12/3	67.2	97.3	97.3
12A	17200	5200	2600	107	12/3	63.4	96.5	96.5

Formulation I
WHITE GLOSS ENAMEL

INGREDIENTS IN ORDER OF ADDITION	DESCRIPTION/FUNCTION	SUPPLIER	GRAMS
BASE:			
Medium Oil Alkyd (11-070)	50 wt. % solution of medium oil alkyd resin and Rule 66 Mineral Spirits	Reichhold Chemicals	106 g
Rule 66 Mineral Spirits	Solvent	Union 67	10 g
Raybo HS57 Optisperse	Dispersant	Raybo	4 g
CR 822 TiO_2	Pigment	Tronox	130 g
High speed dispersed at 7000 rpm using a Dispersmat for 20 minutes			
Medium Oil Alkyd	As above	As above	30 g
Rule 66 Mineral Spirits	As above	As above	30 g
Stirred at moderate speed for 5 mins.			
Organoclay	Thixotrope	—	3 g
Methanol/H_2O(95.5)	Polar Activator	Alrich Chemicals	1 g
Dispersed at 5000 rpm using a Dispersmat for 20 minutes			
LET DOWN:			
Medium Oil Alkyd	As above	As above	50 g
Rule 66 Mineral Spirits	As above	As above	30 g
Cobalt Drier (6%)	Film drier	Interstab	0.7 g
Zirconium Drier (6%)	Film drier	Interstab	1.4 g
Calcium Drier (5%)	Film drier	Interstab	2.5 g
Anti Skinning Agent	Prevent skin formation	Interstab	0.4 g

Formulation II
WHITE GLOSS TOP COAT ENAMEL

INGREDIENTS IN ORDER OF ADDITION	DESCRIPTION/FUNCTION	SUPPLIER	GRAMS
BASE:			
Marine Oil Alkyd (1560M-50)	50% solution of Marine Oil Alkyd and Rule 66 Mineral Spirits	Spencer Kellog	116.6 g
G-Solve	Solvent	Union 67	10 g
Raybo HS57 Optisperse	Dispersant	Raybo	4.8 g

-continued

Formulation II
WHITE GLOSS TOP COAT ENAMEL

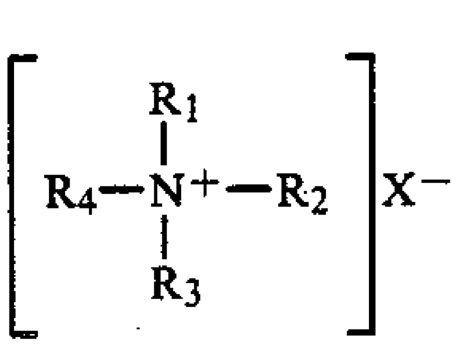
INGREDIENTS IN ORDER OF ADDITION	DESCRIPTION/FUNCTION	SUPPLIER	GRAMS
CR 822 TiO_2	Pigment	Tronox	130 g
High speed dispersed at 7000 rpm using a Dispersmat for 20 minutes			
Marine Oil Alkyd	As above	As above	32 g
Xylene	Solvent	Aldrich Chemicals	32 g
Stirred at moderate speed for 5 minutes			
Organoclay	Thixotrope	—	3 g
Methanol/H_2O(95:5)	Polar Activator	Aldrich Chemicals	1 g
Dispersed at 5000 rpm using a Dispersmat for 20 minutes			
LET DOWN:			
Marine Oil Alkyd	As above	As above	138 g
Hi Flash Naphtha	Solvent	Chem Central	26 g
Lead Drier (24%)	Film drier	Interstab	1.6 g
Cobalt Drier (6%)	Film drier	Interstab	0.64 g
Anti Skinning Agent	Prevent Skin Formation	Interstab	0.64 g

What is claimed is:

1. A process for preparing an organoclay which is readily dispersible in an organic medium, which process comprises:
(a) mixing an aqueous suspension of a smectite clay with a quaternary ammonium compound capable of rendering the smectite clay organophilic in proportions such that there are present from 75 to 110 milliequivalents of quaternary ammonium cation per 100 g of dry smectite clay;
(b) subjecting the mixture formed in step (a) to high shear mixing for a time sufficient to dissipate in the mixture at least 100 KJ of energy per kg. of dry solids in the mixture; and
(c) dewatering the product of step (b).

2. A process according to claim 1, wherein the dewatered product of step (c) is dried and milled.

3. A process according to claim 1, wherein the quaternary ammonium compound can be represented by the general formula:



wherein R_1 is selected from saturated and unsaturated alkyl groups having from 10 to 24 carbon atoms, R_2 and R_3, which may be the same or different, are each selected from saturated and unsaturated alkyl groups having from 1 to 24 carbon atoms and aralkyl groups having at least 7 carbon atoms, R_4 is selected from alkyl groups having from 1 to 6 carbon atoms and aralkyl groups having at least 7 carbon atoms, and X is selected from OH, Cl, Br, I, NO_2, CH_3SO_4 and $CH_3.COO$.

4. A process according to claim 3, wherein the quaternary ammonium compound is selected from the group consisting of benzyl methyl dialkyl ammonium chlorides, dimethyl dialkyl ammonium chlorides, benzyl dimethyl alkyl ammonium chlorides, benzyl trialkyl ammonium chlorides and methyl trialkyl ammonium chlorides in which the one or more alkyl group represents a mixture of hydrocarbon radicals derived from tallow having from 14 to 20 carbon atoms.

5. A process according to claim 4 in which there is used a mixture of dimethyl dihydrogenated tallow ammonium chloride and dimethyl benzyl hydrogenated tallow ammonium chloride as quaternary ammonium compounds.

6. A process according to claim 5 in which a mixture of about 87 mole percent dimethyl dihydrogenated tallow ammonium chloride and about 13 mole percent dimethyl benzyl hydrogenated tallow ammonium chloride is used as quaternary ammonium compounds.

7. The organoclay product prepared by the process of claim 1.

8. The organoclay product prepared by the process of claim 5.

9. The organoclay product prepared by the process of claim 6.

* * * * *